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## CHAPTER 1

### Introduction

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## Abstract

Organic thermoelectric materials and generators are a promising field of research due to numerous attractive characteristics that suggest the ability to overcome the shortcomings of existing inorganic TE systems. This book aims to reprise some of the key directions in this field and provide some context on the key developments and opportunities that remain to be explored. Therefore, to facilitate comprehension of the book, this introduction chapter will present a brief overview of essential topics spanning the fields of chemistry, materials science, engineering, and physics, including a brief historical overview of organic TE materials. TE measurement techniques, including carrier-energy and thermal transport in organic TE systems, will also be briefly be discussed, as they are relevant to understanding what challenges remain in understanding and optimizing the performance of these organic TE materials.

The field of thermoelectrics (TEs) has existed for over 150 years since the Peltier and Seebeck effects were first observed in the mid 19<sup>th</sup> century. Broadly speaking, TEs play a dual role in the broad energy landscape – they have the ability to interconvert thermal and electrical gradients – a connection that no other type of technology can offer. Traditionally, these TE effects have been realized predominantly in inorganic materials, and this has been fruitful for the development of solid state devices of use in mostly niche applications in refrigeration and power generation. However, there has been recent momentum toward exploring so-called “soft TEs” <sup>1, 2</sup> in the past decade that this book aims to capture. This was primarily driven by new developments in organic and hybrid materials, and the observation that new TE transport rules, flexible form factors, and low-cost manufacturing processes are all available in these materials.

This book aims to reprise some of the key directions in this field and provide some context on the key developments and opportunities that remain to be explored. In order to quickly develop functional knowledge of this field, a wide-ranging bundle of skills including chemistry, materials science, characterization methods, and transport physics is needed. The following chapters in this book will cover the intriguing electrical and thermal properties of some featured organic materials and their unique transport characteristics will also be discussed. In addition, various interfacial engineering approaches including molecular—junctionshierarchal architectures, inorganic/organic hybrid interfaces, and organic intercalation metal-organic framework will be introduced.

## Motivation

The long-term consequences of global reliance on fossil fuels have led to a significant need for alternative energy and innovative energy-harvesting technologies. Among them, TE energy conversion may be a key player in the suite of next-generation energy technologies. Because they can directly convert thermal energy, such as waste heat, into useful electrical energy via the Seebeck effect or provide both active solid-state cooling and heating from an applied current via the Peltier effect. This is because at least 60% of primary energy produced in the world is wasted in the form of heat.<sup>3, 4</sup> Home heating, automotive exhaust, and industrial processes all generate an enormous amount of unused waste heat. Energy-intensive industries, such as industrial manufacturing, oil and gas operations, and transportation, operate around the clock and produce enough waste heat to generate over 15 GW of electricity per year.<sup>5</sup> Over the last decade, significant research investments have actually been made in the purpose of waste heat recovery to increase energy efficiency. Several car manufacturers have investigated the impact of converting waste heat to electricity in the automobile engine and have applied TE generators in real automobile production.<sup>6</sup> Some studies targeted the development of TE generators that can be attached onto round-shape hot pipes in plant and to power networking sensors, lights, and portable electronic devices, etc.<sup>7, 8</sup> However, despite significant potential, TE generators have not yet experienced broad commercial deployment due to a number of challenging issues. Commercially available TEs are typically fabricated with rare or toxic inorganic materials (tellurium, selenium, lead, etc.), and possess other common aspects which limit practical utilization: (1) mass production of TE materials due to scarce resources; (2) shape compatibility to uneven or curved surfaces of heat sources due to rigid form factors; and (3) large-area fabrication for mass-energy conversion owing to energy-

intensive fabrication process. To solve these problems, novel TE material design is required to circumvent the aforementioned limitations. From these reasons, soft TE materials, which are typically based on organic materials, are emerging as a promising candidate for the future TE energy conversion technologies.

Organic materials are an especially appealing area of research for TE applications because they typically possess high levels of mechanical flexibility, are composed of earth-abundant materials, are cost-effective, and have shown the ability for scalable manufacturing. The scalable and low cost manufacturing of organic materials (polymers, small molecules, etc.) has been demonstrated throughout history for a vast array of different commercial applications. Organic materials also offer the opportunity for leveraging pre-established device fabrication and processing techniques (roll-to-roll, inkjet, etc.) which would enable the production of lightweight and flexible next-generation TE devices with a many different geometries and designs.<sup>2, 9</sup> Thus, fully realizing the potential of organic TEs would enable the fabrication of robust, light weight, and flexible devices appropriate for a wide range of new applications.

Over the last decade there has been a global proliferation of low-power electronics such as personal, wearable and healthcare devices. TE generators are ideal for this type of device and are expected to be widely applicable as a local power supply that doesn't require the charging or replacement of batteries for wearable electronic devices, sensors, and personal medical and health-care devices.<sup>10</sup> For example, some implantable medical devices such as pacemakers require only 10 microwatts of power for semi-permanent operation without battery replacement surgery.<sup>11</sup> These

applications are quite interesting because human body heat is one of the most abundant and reliable wasted energy sources, which can be conveniently harvested by utilizing TE energy conversion. Given that the average person emits between 100 and 120 W of heat energy into the air,<sup>12</sup> TE offer promising value when compared to the operational power needs of a smartphone (5 W) or laptop (45 W).<sup>13</sup> Although there is clearly opportunity for the implementation of TE devices, significant progress in the TE generator for wearable applications has lacked thus far. One significant challenge faced by most traditional inorganic TEs is the inherent curvature of the human body and the need for high flexibility and durability in order to insure tight and stable attachment of the device to the skin. Additionally, traditional inorganic TEs are incompatible with wide-area manufacturing techniques that would be essential for maximizing energy conversion. Therefore, especially for wearable applications, organic TE materials have many advantages such as flexibility, light-weight, and processability beyond the intrinsic properties of inorganic TE materials despite the low TE performance.

In summary, organic TE materials and generators are a promising field of research due to their many attractive characteristics that suggest the ability to overcome the shortcomings of existing inorganic TE systems. In the following sections, we will present a brief overview of essential topics spanning the fields of chemistry, materials science, engineering, and physics, including a brief historical overview of organic TE materials. TE measurement techniques, including carrier-energy and thermal transport in organic TE systems, will also be briefly be discussed, as they are relevant to understanding what challenges remain in understanding and optimizing the performance of these organic TE materials.

## History of TE materials: past to present and future

Historically, all commercially available TE generators have been based on doped narrow-bandgap semiconductors. A prototypical example of a high-performance TE material is bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ), discovered by H. J. Goldsmid and coworkers in the U.K. in 1954.<sup>14</sup> The majority of basic theory and common design standards established for TE systems are based on these types of inorganic systems. In the early 1990s, M. S. Dresselhaus and L. D. Hicks proposed an innovative theory that low-dimensional materials are favorable for enhancing material efficiency.<sup>15, 16</sup> This theory predicts that certain materials such as bismuth, which is a poor bulk TE material, can realize high TE performance in 2D quantum-well or 1D quantum-wire structures.<sup>17, 18</sup> After the 2000s, owing to improvement of atomic-scale synthesis and fabrication techniques, new categories of materials with high TE performance such as skutterudites, clathrates, half-Heuslers and quantum dot superlattices have been reported.<sup>19, 20</sup> As a leading TE material, inorganic semiconductors such as the bismuth-tellurium-antimony-selenium (Bi-Te-Sb-Se) alloy family have been widely investigated so far. However, despite their promising TE performances, mechanical brittleness, energy-intensive processing methods, and material scarcity remain critical obstacles for further commercial deployment.<sup>2</sup>

Organic TE materials on the other hand, have attracted increasing amounts of attention throughout the years in an effort to overcome the challenges faced by inorganic TE materials. These “soft” TE materials are exciting for a number of



reasons; they demonstrate novel and unique transport mechanisms and also enable the development of conformal devices that leverage low manufacturing costs. Organic materials including conjugated polymers, polythiophene derivatives, nanoscale carbon-based materials, graphene derivatives, and assorted organic-inorganic hybrid materials have emerged as promising TE alternatives owing to their unique advantages including facile processability, scalability, and flexibility as well as low cost and weight.<sup>2, 9</sup> These organic TE materials have been overlooked for the past decades due to their comparably low TE performance, however, recently huge progress on molecular design strategy, nanostructuring, and fabrication techniques are brightening their future. The following section will touch on some important classes of organic TE materials and provide some historical context.

In the early stage of organic TE research, conjugated polymers such as polyacetylenes, polyanilines, polypyrroles, polyphenylenevinylenes, and metallated polymers were studied due to their reasonable electrical conductivity, good chemical stability, and easy processability.<sup>21</sup> Conjugated polymers are organic macromolecules that are characterized by a backbone chain of alternating double- and single bonds. Their overlapping p-orbitals create a system of delocalized  $\pi$ -electrons, which can result in high electronic conductivity.<sup>22</sup> For example, the heavily doped polyacetylene with iodine demonstrates an electrical conductivity of  $10^4$  S/cm which is comparable to the  $10^5$  S/cm range that copper exhibits.<sup>23, 24</sup> However, low Seebeck coefficients and inefficient fabrication techniques have been critical barriers to the application. Considering this historical background, development of innovative fabrication techniques, which will be introduced more thoroughly in ~~chapter~~Chapter 7 by Prof. Kun Zhang, is an interesting topic worthy of further exploration.

Another family of promising candidates within the organic field are polythiophene-derivatives. Polythiophenes have historically demonstrated low Seebeck coefficient and low electrical conductivity, but recent work on molecular design has resulted in derivatives with high TE performance. Among them, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most popular and high-performing organic TE materials.<sup>25-27</sup> Especially worth noting, PEDOT with poly(styrenesulfonic acid) as a counter ion (PEDOT:PSS) has been commercially applied as a hole-transporting interfacial material in organic photovoltaics/OFETs and as conducting electrodes for various organic-based electronic devices owing to its convenient solution processibility and good stability.<sup>28</sup> Currently, various doping and de-doping processes have been reported with high TE performance. Interestingly, although termed as a doping process, observed TE performance enhancement is mainly due to increased transport efficiency via aligning of backbone chains rather than dramatic changes in carrier concentration.<sup>27, 29</sup> More details on these approaches will be discussed in ~~chapter~~ Chapter 8 by Prof. Jianyong Ouyang.

Since the first discovery by Iijima about three decades ago,<sup>30</sup> carbon nanotubes (CNTs) have attracted tremendous attention due to their superior electronic, thermal, and mechanical properties, and many potential applications such as stretchable soft electronics and energy conversion and storage devices have been explored.<sup>31</sup> Typically, CNTs demonstrate p-type TE behavior in ambient conditions, meaning holes are the major charge carriers. But as it turns out, pristine CNTs are intrinsically electron rich (n-type) materials, and exhibit a negative Seebeck coefficient under vacuum conditions.<sup>32</sup> This phenomenon can be explained by knowing that CNTs are

electron deficient (p-doped) when exposed to ambient oxygen, resulting in conversion from semiconducting CNTs to metallic CNTs behavior.<sup>33</sup> By similar methods, it is possible to easily control CNTs dominant carrier type and carrier concentration by employing various chemical dopants.<sup>34</sup> This flexible p-type to n-type transition is desirable for expanding its potential TE applications and research scopes. Also, its TE performance can be dramatically increased by enhancing the mobility along the direction of the CNTs, or by lowering their diameters to decrease the thermal conductivity.<sup>35</sup> TE behavior of n- and p-type CNTs will be described in [chapter-Chapter 5](#) by Prof. Kamal Kar.

Hybrid organic-inorganic materials are another area of material research that enables pairing the high performance and durability of the inorganic component with the inherent cost-effectiveness and flexibility of the organic component. Especially intriguing is the fact that certain hybrid materials are not only enabled to fabricate via solution processable printing or casting but also have demonstrated synergistic effects where the hybrid material performance surpasses the additive performance of either of the initial parent components. The exact physical mechanism underlying these synergistic enhancements is unclear, but an active topic of inquiry in the TE community. Some competing hypotheses have garnered traction of late, including energy filtering, morphological and interfacial charge transfer effects, amongst others.<sup>36-38</sup> Further examination of both the theoretical and experimental nature of this synergistic phenomenon will be discussed in [eChapter 9](#) [by Prof. Lidong Chen](#).

In addition, one area of hybrid material research that has yielded very promising results is the intercalation of organic molecules into layered inorganic materials.<sup>39, 40</sup> This strategy, yields materials that demonstrate TE performance approaching that of

state-of-the-art inorganic materials while maintaining the appeal of low thermal conductivity and flexible form factors that incorporating organic species impart.<sup>40</sup> This emerging approach will be introduced in [eChapter 12](#) by Prof. Shiren Wang.

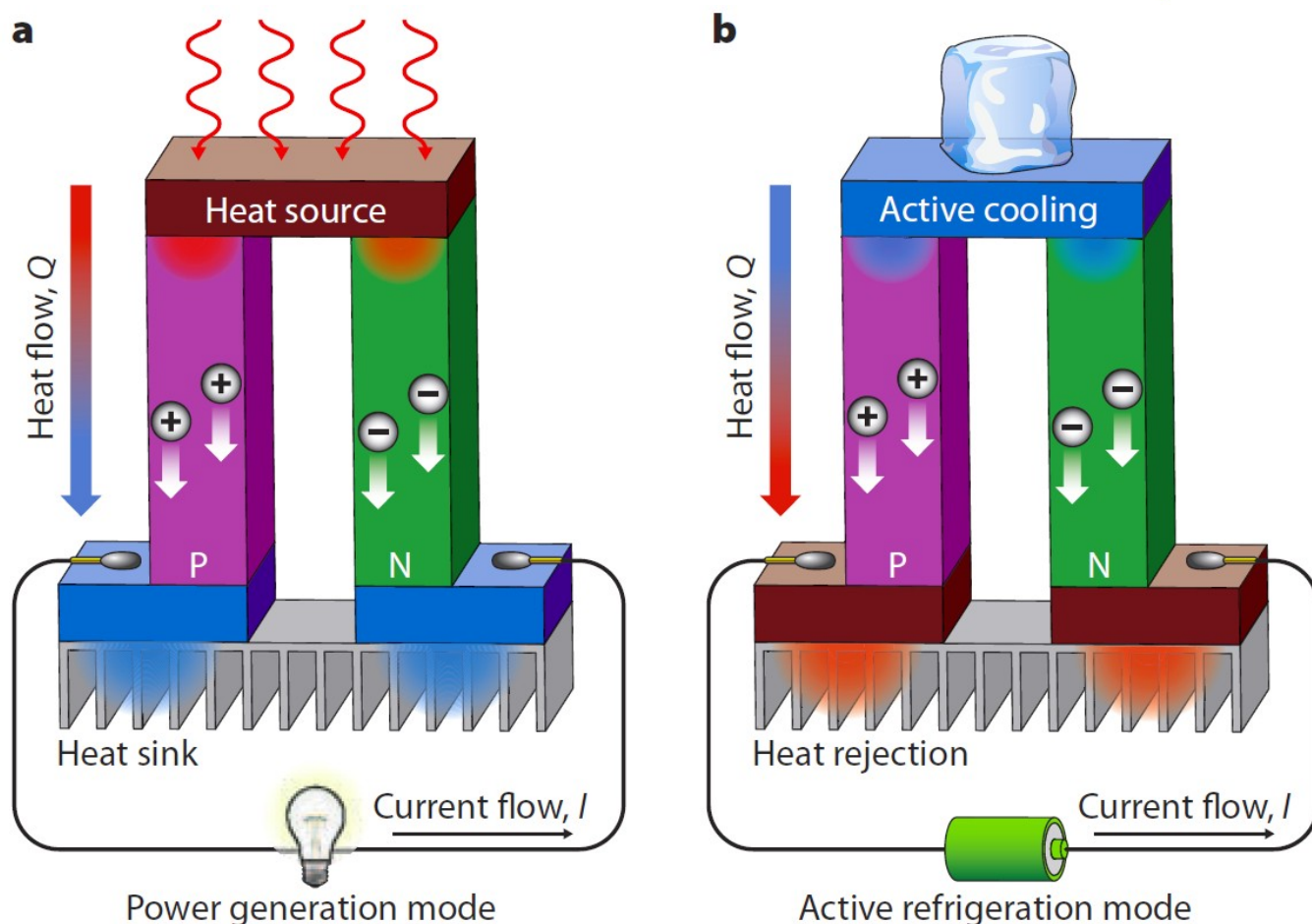
The materials mentioned thus far have undergone extensive study and yet there is still a notable lack of understanding when it comes to the underlying fundamental physics responsible for the performance and transport observed. The study of molecular junctions offers an alternative approach for probing structure-function relationships by inspection of ultra-simplified model systems. Specifically, researchers have been able to reproducibly create junctions composed of a single organic molecule; this simplifies the problem, making it possible to garner a firmer grasp on the physics due to the reduced number and complexity of molecular orbitals participating in charge transport. In addition to the understanding gained through the study of these sorts of molecular junctions, research has also suggested that the most efficient TE transport takes place in these sorts of systems.<sup>41, 42</sup> Molecular junctions make it possible to not only precisely control the properties and doping levels of each material, but also to fabricate numerous TE junctions for maximizing TE performance of the module. Building electrical components and interconnects using single molecules has been explored in the electronic community and molecular junctions have also been studied for constructing feasible molecular devices with desirable electrical and thermal transport characteristics. However, despite its appeal in unveiling basic physical principles, one should not mistake this area of scholarship for an established technology. Single molecule TE studies have been unable to produce high TE performance and realistic products for real applications but they have, however, contributed greatly to our understanding of TE transport in organic systems.

The orbital view – contrasted with the band view of TEs – will be expanded upon in Chapters 2 and 3 by Prof. Ling Li and Hui Xu, will provide a lot of insight for future research efforts aimed at molecular design of optimum TEs.

In order to give readers a better understanding of the topics to come, the next section of this introductory chapter will focus upon presenting the basic principles of TEs, and covering concept and performance evaluation of TE materials and modules.

### **Thermoelectrics: basic principles**

TE modules are direct heat to electricity converting devices. The way in which they operate is that when a thermal gradient is applied to a TE material, carriers spontaneously flow from hot region to cold region, thereby current can be produced by the carriers and ultimately a voltage potential ( $\Delta V$ ) arises across the material via the Seebeck effect.(Fig. 1a) Conversely, if the current is applied, exothermic and endothermic reactions can occur at the semiconductor-metal junctions via the Peltier effect.(Fig. 1b) Generally, a TE device starts with a pair of n- (electron rich) and p-type (electron deficient) semiconducting materials are known as a TE couple and a practical TE generator consists of multiple pairs of p-type legs and n-type legs. When many elements are arranged electrically in series and thermally in parallel, the operating voltage of the module rises and current decreases. Such an arrangement minimizes parasitic losses due to the serial electrical resistance of wires and interconnects.



**Figure 1.** Schematic illustrations of a thermoelectric module for (a) power generation (Seebeck effect) and (b) active refrigeration (Peltier effect). (a) An applied temperature difference causes charge carriers in the material (electrons or holes) to diffuse from the hot side to the cold side, resulting in current flow through the circuit. (b) Heat is absorbed at the upper junction and propagates to the lower junction when a current is made to flow through the circuit. Reproduced from Ref. 43 with permission from Springer Nature, [<https://doi.org/10.1038/asiamat.2010.138>].<sup>43</sup>

The TE performance of materials is evaluated by a dimensionless figure of merit ( $ZT$ ), which is given by

$$ZT = \frac{S^2 \sigma}{\kappa} \quad (1)$$

where  $S$ ,  $\sigma$ ,  $T$ , and  $\kappa$  are the Seebeck coefficient (also known as thermopower), electrical conductivity, absolute temperature, and thermal conductivity, respectively. These parameters are determined by the details of the electronic structure and scattering of charge carriers (electrons or holes), unique to each material system and thus are not independently controllable. The Seebeck coefficient reflects the average entropy that can be transported per charge carrier and thus decreases with increasing carrier concentration. By contrast, the electrical conductivity increases with carrier concentration,  $n$ , because  $\sigma = e\mu n$  where  $e$  is the electronic charge and  $\mu$  is carrier mobility. The thermal conductivity  $\kappa$  has contributions from carrier and lattice vibrations,  $\kappa = \kappa_{\text{lattice}} + \kappa_{\text{electronic}}$ ; the electronic contribution increases with carrier concentration, as charge carriers can also transport heat. While these parameters are dependent upon the material being measured, there is the added challenge that these properties are also intrinsically linked in such a way that they are often inversely related, thus optimization of  $ZT$  can be quite challenging.

## Charge-carrier transport

Energy transport in organic systems can vary drastically from transport within periodic inorganic systems due to their lack of long-range structural order and decreased orbital overlap. The inherent periodic nature of inorganic systems leads to well-defined energy transport via states existing within continuous energetic bands. Conversely, organic electronic systems tend to be studied existing in varying states of disorder. As a result, carriers are typically forced to hop from one discrete localized state to another. The main transport pathway in an organic system is the conductive

backbone of the molecule or polymer. However, due to the fact that organic systems are typically comprised of distinct molecules, eventually, the carrier will be forced to move to another backbone in order to continue its conductive progression. Bonding between separate backbones tends to be comprised of far weaker interactions such as van der Waals bonding which ultimately causes a significant energetic barrier for carriers to move throughout the sample even in systems with fairly high levels of crystallinity.<sup>44</sup> Pi ( $\pi$ ) stacking is one type of ordering of organic molecules or polymers that typically enables the best “communication” between isolated organic bodies. It can occur when individual molecules stack in such a way that enables electronic overlap of their conjugated  $\pi$  orbitals. This type of stacking seems to ultimately be the most electronically effective form of organization for conjugated organic molecules.<sup>2</sup>

As a result of poor long-range electronic transport, the electronic structure for an organic molecule or polymer is often represented as individual states with a highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The HOMO can generally be likened to the valence states found in an inorganic semiconducting system and the LUMO to the conduction states.<sup>2</sup> The weak interaction between individual organic molecules or chains causes a shift in modeling approaches from inorganic systems. The reality for organics is that the energetics for the entire system can usually be best described by the energetics of the individual molecule or more broadly as a Gaussian density of states.<sup>2, 44</sup>

Another difference between traditional inorganic semiconducting systems is the fact that electrons and holes are not always the majority charge carrier in organic systems. Polarons, a type of quasi-particle made up of a charged species paired with a phonon, are often times the dominant species of charge carrier in disordered organic



systems.<sup>44, 45</sup> Polarons come about from electrons being added or removed to an organic molecule's conjugated  $\pi$  orbitals which then leads to structural distortion in the backbone.<sup>2</sup> The existence of these quasi-particles can cause a decrease in mobility in the system due to a heavier polaron effective mass and the increased likelihood of carrier self-trapping.<sup>44</sup>

Bipolarons are another type of quasi-particle that exists and can dominate transport within organic systems. A bipolaron is defined as two like-charges localized by interaction through a lattice distortion.<sup>46</sup> These quasi-particles can exist because the alignment of the two similar charges relaxes the lattice distortion previously induced by the formation of a polaron. The energy payoff that results from the lattice relaxation is larger than the inherent Coulombic repulsion that occurs between the two like-charges. Bipolarons are similar to polarons but have differing effects upon transport, both can be monitored in organic systems via optical absorbance spectroscopy.<sup>2</sup> The result of polarons and bipolarons existing within organic systems adds an additional layer of complexity to understanding the overarching energy transport landscape in organic systems. Linear trends in the relationship between conductivity and doping concentration are less likely due to the challenge of inherent disorder causing increased scattering events and the formation of polarons and bipolarons causing deformations in molecular scale packing.

## **Electrical Conductivity and Seebeck Optimization**

Organic materials tend to exhibit inherently low thermal conductivities, as a result, it is common practice to focus primarily upon increasing the power factor of the organic

material.<sup>2, 47</sup> Typically, increasing the electrical conductivity is the most straightforward and effective approach to maximize TE performance. Most organic semiconductors, usually exhibit very low electrical conductivity due to large gaps between their HOMO and LUMO levels, thus doping is necessary to induce a reasonably high level of TE performance.<sup>46</sup> Electronic levels in these systems are a result of the molecular ionization energy and electron affinity which can both be tuned by molecular design and doping.<sup>2</sup> Doping, however, is not the only influential factor for boosting conductivity, due to the high concentration of trap states, carrier mobility is another crucial factor.<sup>48</sup> It should also be noted that both carrier concentration and carrier mobility are coupled, thus often times increasing carrier concentration can cause a decrease in mobility due to an increased probability of scattering events between carriers. More highly ordered systems usually exhibit stronger  $\pi$  orbital overlap leading to higher mobility which often times can be more beneficial for boosting conductivity than increasing carrier concentration would.<sup>46, 47, 49, 50</sup>

Electrical conductivity is not the only challenging TE parameter to understand in organic systems. The Seebeck coefficient has a direct dependence upon temperature, however drawing clear trends can be challenging due to variable transport mechanisms. It is possible to loosely establish temperature dependence trends once differentiating systems based upon degree of disorder.<sup>2</sup> In highly disordered systems the Seebeck shows temperature independent behavior where transport is assumed to be dominated by thermally assisted hopping, whereas in highly ordered systems the Seebeck coefficient shows an increase with rising temperature where transport occurs via band-like conduction. While this type of behavior may seem contrary to what would be expected in organics, in reality it simply demonstrates the wide range of

transport, from insulating to nearly metallic, that can be found in these materials. Systems that display a mixture of crystalline and amorphous structures demonstrate a complex relationship between temperature and Seebeck coefficient due to mixed types of transport within such a system.<sup>2</sup>

Techniques to enhance the Seebeck coefficient borrow from those established for increasing electrical conductivity. Due to the Seebeck coefficient's inverse relationship to electrical conductivity, it is usually safe to assume that decreasing performance of one property in an organic system will lead to an increase in performance in the other. Ultimately, several different techniques can be employed to enhance the Seebeck coefficient of a system without a significant decrease in electrical conductivity. Two common techniques for enhancing the Seebeck coefficient through introducing higher degrees of asymmetry about the Fermi level are energy dependent filtering and tuning the shape of the electronic DOS. Energy dependent filtering is said to come about as a result of employing interfacial engineering between two dissimilar energetic entities.<sup>51, 52</sup> This effect is a point of contention within the field of TE materials due to the challenges associated with direct experimental verification of the phenomenon, some groups have even gone so far to suggest that the role of energy dependent filtering is highly overstated in the literature.<sup>38, 53</sup> The second technique utilizes the addition of different species which causes a change in the ionization energy of the entire system, thus resulting in a narrowing of the DOS.<sup>49, 54, 55</sup>

Additionally, solubility and stability should be considered in order to impart ease of processability and device longevity. Adding different functional moieties to organic molecules or polymers is a common synthetic technique appealing for imparting

solubility and stability to the system but ultimately the added functional groups can act as insulators and decrease the overall mobility and conductivity of charge carriers within the system.<sup>56</sup> This inverse relationship between performance and processability is one of the challenges facing organic TE materials.

The strategies detailed above are effective but ultimately are still lacking to produce widespread performance surpassing inorganic materials. One such weakness faced when dealing with organic systems is the challenge in developing effective models, due to the complexity and irregularity of energy transport in these systems. Some hopping or mobility edge models do exist but their effective deployment is limited. Only recently has the first universal TE transport model for conducting polymers been proposed.<sup>57</sup> This model, developed by Kang and Snyder, provides experimentalists with tools to understand the role of key material parameters, such as carrier concentration and morphology, in TE transport trends within organic systems. While this model is quite promising, there are still many aspects of carrier dynamics and charge transport within these complex organic systems that are poorly understood.

## **Thermal transport**

Organic materials typically exhibit very low native thermal conductivity values compared to inorganic TEs, which translates into the ability to maintain a large temperature difference that is beneficial to achieving higher ZT values. Thermal transport, quantified as thermal conductivity, is a combination of heat conduction of phonons (lattice vibrations) and heat transported by electrons and holes (e.g., heavily doped materials and conductive polymers). Furthermore, the electronic contribution

to thermal transport is nearly negligible for undoped organic semiconductors, due to low carrier concentrations, when compared with the phonon contribution. With lattice vibrations being the major contributor to thermal conductivity in the system, organic TE material's lack of long-range structural order and non-covalent bonding interactions typically results in a significant reduction of the mean free path (distance traveled before scattering) of phonons. This impediment is one of the causes leading to the relatively low thermal conductivity of organic materials which is typically below  $1 \text{ W m}^{-1}\text{K}^{-1}$ , a range that is approaching the lower limit of thermal conductivity of inorganic TEs.<sup>9</sup>

In general, nanostructured materials and materials employing interfacial engineering can show reduced thermal transport without a great detriment to electrical conductivity. This effect comes about due to the differences between electron and phonon mean free paths; phonons typically exhibit much longer mean free paths than electrons,<sup>58</sup> therefore through careful control of the size of the transport pathway, it is possible to constrain dimensionality to the point where electrons can move unencumbered but phonons are scattered at interfaces.<sup>59</sup> An alternative approach for decreasing thermal conduction is the utilization of mesoporous materials. These materials have high porosity which causes a reduction in the possible phonon transport pathways with little detriment to electrical conductivity.<sup>60</sup>

## **Module performance and design**

Currently, there are commercial TE devices available on the market and extensive effort has been spent on designing and optimizing these modules. These devices can

realize both power generation and solid-state cooling but are suitable exclusively for rigid, brittle, inorganic materials. With the advent of high performing soft organic materials, one would assume that extensive research might have been done into exploring the new possibilities for device optimization for this new class of materials. This, however, has not been the case, with the design of flexible TE devices still being in its proof-of-principle stage. In spite of efforts to improve organic TE material performance, the TE organic module is relatively low performing when compared to conventional power cycles and inorganic TE modules. In order to maximize the organic TE device, proper module design and geometry, that capitalize upon the benefits of lightweight, flexible soft materials, must be selected.

As an effort to improve the performance and commercialize TE modules, the general design strategies for TE modules, usually inorganic materials, are well established. Module performance is not only dependent on material properties but also leg geometry and leg spacing. In the design of a TE module, both system performance (electrical power output in generators and cooling power in coolers) and efficiency should be considered together. At a fixed geometry of the legs, achieving maximum power output and efficiency together is impossible. In general, the power output increases as the legs become shorter (low internal resistance) from reducing losses from Joule heating. However, higher conversion efficiency is achieved at longer leg lengths. In other words, the optimal TE module is eventually designed under the nature of a trade-off between  $P_{max}$  and  $\eta_{max}$ .

There have been a lot of studies to optimize the length<sup>61-64</sup>, cross sectional area (or fill factor),<sup>65-68</sup> and the number of pairs of TE materials.<sup>62, 69, 70</sup> The fill factor is the fraction

of total available space in a module taken up by TE legs. The studies have shown the geometric parameters of TE modules are interconnected to each other for the optimization and take a critical role to change the performance by an order of magnitude. Furthermore, since the performance of TE modules is low compared to the conventional power generating or cooling cycles due to the materials limit of ZT, the modules require a systematic approach to optimize the whole system including heat exchangers,<sup>71-74</sup> coupling with TE modules,<sup>75-78</sup> and the thermal and electrical contact resistance at interface layers.<sup>79-81</sup> In order to properly utilize the electricity from TE generators, there also have been studies on electrical converters and algorithms for the electrical operation points.<sup>82-85</sup>

To date, TE modules have mainly been realized in two representative architectures: a. vertical geometry and b. planar geometry as shown in Figure 2.<sup>2</sup> The vertical geometry consists of two legs in two dimensions over a substrate with patterned electrical contacts. The thermal gradient across the materials is perpendicular to the substrate. This geometry is mainly adopted in commercial TE modules with typical inorganic materials. The planar geometry has been introduced from the advance of thin film technology and large area fabrication methodology.<sup>86, 87</sup> The thermal gradient across the TE materials in this geometry is parallel to the substrate. Although single leg modules exist, alternating n- and p- type legs electrically in series and thermally in parallel makes for better interconnects, decreases parasitic thermal leakage and enables large voltage generation.

**Figure 2.** (a) Vertical architecture for TE modules. Traditional inorganic TEGs typically comprise rigid, pillar-like p n legs tiled over a ceramic substrate and require a thermal gradient incident perpendicular to the substrate. (b) Planar architecture for TE modules. Soft TEs are typically patterned in 2D onto a flat substrate using low-cost, scalable printing techniques. For the planar architecture, a thermal gradient can be applied parallel to the substrate, rendering optimization and understanding of in-plane carrier transport key for these materials. (c) The 2D planar architecture are transformable into flexible and lightweight 3D structures ideal for wearable applications. Reproduced from Ref. 2 with permission from Springer Nature, [<https://doi.org/10.1038/natrevmats.2016.50>].

Each architecture has advantages and disadvantages regarding fill factor, thermal losses, and geometric constraints.<sup>88</sup> Vertical architectures benefit from high packing density, which enables high thermovoltages. However, the vertical legs limit how thin the module can be made, which makes this architecture less ideal for applications that demand thinner geometries. On the other hand, planar architectures suffer from a low fill factor and parasitic thermal losses through the substrate, thus resulting in low output voltages and degraded device efficiency. Nevertheless, this inherently thin structure is particularly appealing for organic TE modules due to its potential for achieving a high degree of flexibility, which can be more easily integrated into wearable and conformal applications.



Based on the flexibility of organic materials, organic TE modules mostly adopt a planar architecture which leverages inexpensive solution based processing techniques, enabling the reliable patterning of 2D arrays of TE legs. Organic TEs are especially appealing for flexible devices that enable conformal contact with the human body for either power generation or thermal management capabilities in a wearable, textile-based form. An additional area of appeal is the potential integration into low temperature applications that utilize a wide range of different fabrication techniques such as large-area printing, 3D printing, spray coatings, etc. In order to overcome the low fill factor of planar modules, folding techniques have been discussed to transform the 2D array into lightweight 3D architectures with a variety of geometries. ~~The more specific issues for fabricating polymer based TE generator will be detailed in Chapter 7 by Prof. Kun Zhang.~~

## Measurement techniques for organic TE materials

Accurate measurement of TE properties is a crucial topic for the systematic study of organic TEs. Ultimately it would be challenging to introduce all measurement techniques here owing to the wide range of organic TE materials with various dimensions and performances, from molecular junctions to highly-ordered polymers. Therefore, only the most common measurement techniques and a brief description of each will be presented herein.

The measurement of TE properties involves several sub-measurements: electrical conductivity, the Seebeck coefficient, and thermal conductivity. Among those three properties, the measurement of electrical conductivity is relatively straightforward through the common linear 4-probe method with bar-shaped samples. Electrical current is introduced from one end to the other while the voltage is being measured at another two intermediate points. However, the electrical conductivity is highly sensitive to errors in the geometric factor which can easily be in excess of 5%.<sup>89</sup> Another popular technique that is less sensitive to this error in geometric factors is the van der Pauw technique.<sup>90</sup> The resistivity is obtained from a flat sample of arbitrary shape but uniform thickness with point contacts along its circumference.

The Seebeck coefficient is typically measured by inducing a uniform temperature gradient across a sample while simultaneously monitoring the sample temperature and resulting voltage potential between hot side and cold side. The temperature is traditionally monitored via thermocouples in direct contact with the sample and the voltage potential monitored by electrical probes. Errors in this measurement have a huge impact upon the overall ZT value due to the Seebeck coefficient being squared in the numerator. During the measurement, the applied temperature difference should be modest in order to ensure the measurement is performed within a linear Seebeck regime, as mentioned previously the Seebeck coefficient has a non-linear dependence upon temperature.<sup>89</sup> Organic semiconductors normally have a small electrical conductivity, so the measurement of an accurate Seebeck coefficient will require special consideration, such as using a low noise voltmeter with ultra-high input impedance. For the measurements of Seebeck coefficient and thermal conductivity,

careful consideration of possible heat loss due to the requirement of temperature measurement is needed.

Accurate and precise measurement of thermal conductivity is one of the most crucial and challenging parts of organic TE characterization. Various methods for thermal conductivity measurement are developed depending on the sample size and the desired temperature range.<sup>9, 91</sup> There are four most widely utilized methods, the laser-flash method, three-omega ( $3\omega$ ), time domain thermal reflectance (TDTR) and micro-thermal bridge method.<sup>92, 93</sup> The laser-flash method is most often applicable for macroscopic bulk samples and samples with a thickness down to 100  $\mu\text{m}$ . For thin film geometries  $3\omega$  and TDTR are most useful but both techniques necessitate the deposition of a nanometer thick metallic layer to aid in accurate measurement which can ultimately cause the intrinsic thermal properties of the sample to be masked. The micro-thermal-bridge method is used to measure one-dimensional nanowire (1D NW) like samples. Among these techniques, the laser-flash method is fast, versatile, has a wide measuring range that can be realized by many commercially available instruments. Organic TE modules are typically fabricated as a thin film substrate, for which conventional methods for bulk samples will not be very practical. Unfortunately, the techniques for measuring samples with smaller sizes are not as robust and face challenges when measuring both in-plane and out-of-plane thermal conductivity. This lack of both in- and out-of-plane measurement is especially concerning for organics given their high degrees of anisotropy. Despite these challenges, thermal conductivity measurements are critical for accurate characterization of TE efficiency. Therefore, further development of measurement techniques applicable to a wide range of sample sizes, morphologies and geometries is essential.

In conclusion, ensuring accurate measurement of TE properties is essential not only for reporting reliable results but also for garnering a better grasp of the fundamental physics arising in the organic TE system. While electrical conductivity and Seebeck coefficient measurements are fairly well established it is essential that the TE community is constantly striving towards more accurate and precise measurements. The true challenge, however, lies in reproducible and robust thermal conductivity measurements. Due to organics' traditionally low thermal conductivity and the challenge associated with thermal measurements, there has been a notable lack of reporting thermal conductivity in the organic literature. This is a major challenge and is likely a contributor to the impediment of organic TE device deployment commercially. This area as a whole requires further thought and design before it will be possible to gather accurate values for describing thermal transport in organic TE systems.

## **Perspective**

Imagine a future where small wearable health monitoring devices are powered by body heat and smart clothing could cool you on a hot day. As electronic devices have become more ubiquitous and require more functionality, both TE generators and Peltier coolers would have huge potential in wearable uses. Flexible and robust TE generators can also play an important role as an efficient local power supply for the wasted heat recovery in real life. Up to now, most commercial TE studies and applications have been mainly carried out with inorganic materials due to their high performance, however, their intrinsic

brittleness is a critical obstacle for wearable applications and shape compatibility of uneven heat source surfaces. For these innovative applications, novel functions such as flexibility, portability, and durability of TE modules are essential. Organic TE technologies are one of the most promising avenues to realize such a dream.

Of course, organic TEs still require significant progress to make before being deployed into the commercial market. Understanding and enhancing performance in these complex systems remains quite challenging due to a tangible lack of fundamental insight into the charge transport in these materials. Therefore, it is essential that equal attention is paid to both enhancing TE performance and to establishing more understanding of the fundamental science. In addition to the need for material performance enhancement and understanding, there is also a pressing need for new conceptual advances in module design. It is an unnecessary restriction that device geometries initially intended and optimized for rigid, inorganic systems are utilized for these new innovative, flexible materials. For example, rather than employing traditional methods for building 3D modules, new techniques have been developed, such as patterning conductive inks onto flexible substrates to form 2D conformal arrays that can then be constructed into more complex 3D architectures.<sup>??</sup> Organic materials offer the opportunity for completely re-imagining TE devices to leverage the benefits of flexible, conformal, and solution processable materials in such a way that enables a whole host of exciting new applications. It is apparent that through a combination of material optimization and device innovation, the path to

widespread deployment of organic TEs is possible. Ultimately, although organics have demonstrated performances comparable to that of their inorganic counterparts, the field of organic TE materials and devices remains in its infancy, however, with a very bright future ahead. We hope that this book will provide useful insight and guidance to its readers.

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## Figure captions

**Figure 1.** Schematic illustrations of a thermoelectric module for (a) power generation (Seebeck effect) and (b) active refrigeration (Peltier effect). (a) An applied temperature difference causes charge carriers in the material (electrons or holes) to diffuse from the hot side to the cold side, resulting in current flow through the circuit. (b) Heat is absorbed at the upper junction and propagates to the lower junction when a current is made to flow through the circuit. Reproduced from Ref. 41 with permission from Springer Nature, [<https://doi.org/10.1038/asiamat.2010.138>].<sup>43</sup>

**Figure 2.** (a) Vertical architecture for TE modules. Traditional inorganic TEGs typically comprise rigid, pillar-like p n legs tiled over a ceramic substrate and require a thermal gradient incident perpendicular to the substrate. (b) Planar architecture for TE modules. Soft TEs are typically patterned in 2D onto a flat substrate using low-cost, scalable printing techniques. For the planar architecture, a thermal gradient can be applied parallel to the substrate, rendering optimization and understanding of in-plane carrier transport key for these materials. (c) The 2D planar architecture are transformable into flexible and lightweight 3D structures ideal for wearable applications. Reproduced from Ref. 2 with permission from Springer Nature, [<https://doi.org/10.1038/natrevmats.2016.50>].

## Figures

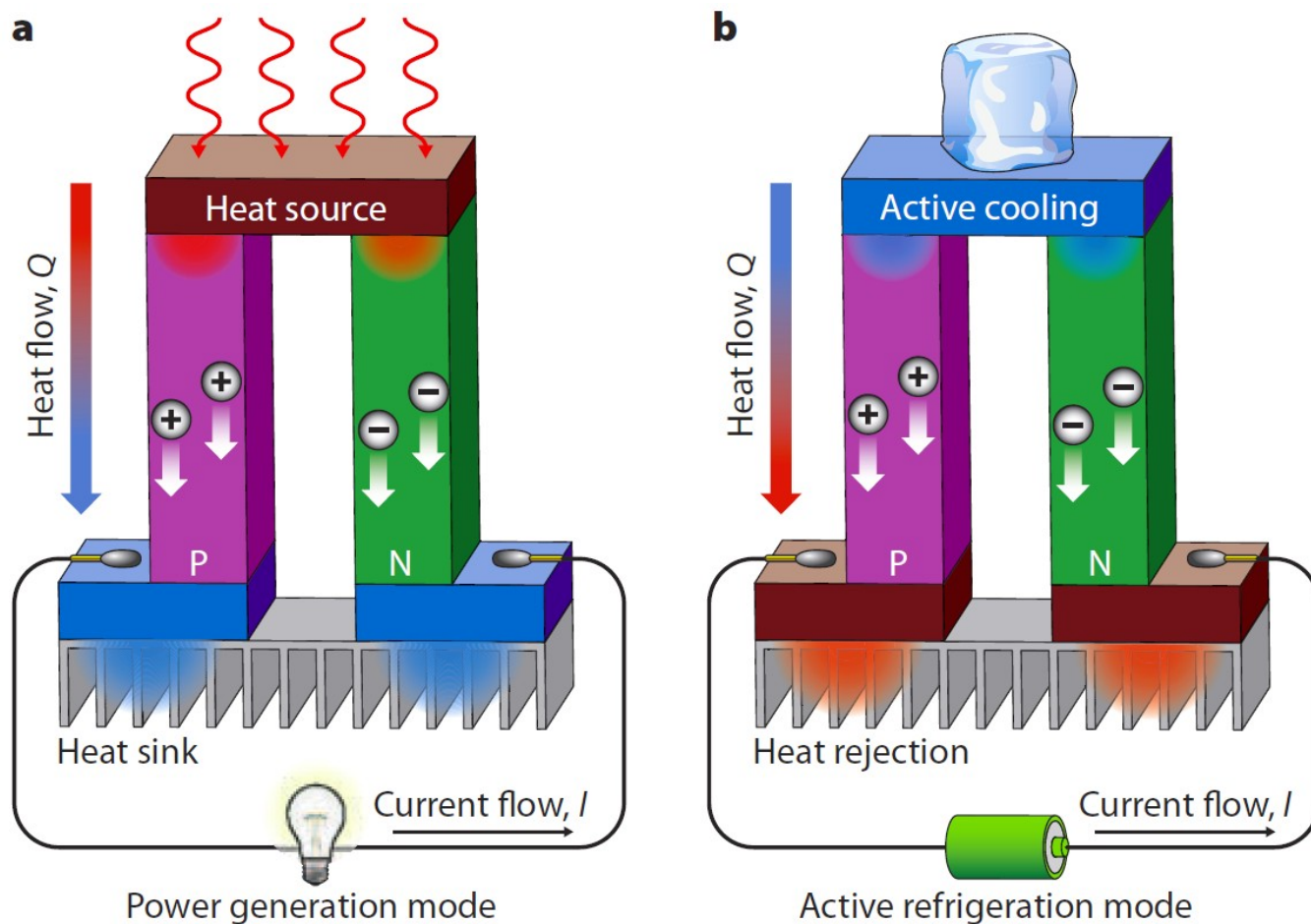


Figure 1.

Figure 2.